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A Report on Work Sponsored by

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Contract N00014-78-C-0147
NR093-052/11-11-77 Code 473
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March 1979

Fluorochem, Inc.
680 South Ayon Ave.
Azusa, California 91702

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HIGH ENERGY HALOGEN CHEMISTRY

by

K. Baum, P.T. Berkowitz and A.M. Guest

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Triflates	Polymerization
2-Fluoro-2-nitrooxetane	Analysis-hydroxyl determination
2-Fluoro-2-nitro-1,3-propanediol	Nuclear magnetic resonance spectra
2-Fluoro-2,2-dinitroethyl glycidyl ether	Infrared spectra
1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Evidence was found that the dimerization of 2-fluoro-3-hydroxy-2-nitro-1-propyl tosylate proceeds via deformylation and elimination to 1-fluoro-1-nitroethylene. Adducts were obtained of dimethyl malonate and of sodium methoxide with this olefin formed *in -situ*.

The reaction of 2-fluoro-2,2-dinitroethanol with 2-fluoro-2-nitro-1,3-propylene ditriflate gave 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane.

The yield of 2-fluoro-2-nitro-1,3-propanediol from diethyl fluoronitromalo-

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20. ABSTRACT (cont'd.)

nate was improved to 70%. A new route to this alcohol was found by the reaction of fluorodinitroethyl triflate or tosylate with alkaline formaldehyde. A one step synthesis of the diol was obtained by adding p-toluenesulfonyl chloride to fluorodinitroethanol in alkaline formalin. The trimethylsilyl group was shown to be a convenient derivative for purification of the diol.

Efforts to prepare oxetanes from 2,2-dinitro-3-hydroxy-1-propyl triflate, 3-hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate, or oxazolidone derivatives under mildly basic conditions were unsuccessful.

The polymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether and its copolymerization with 3-fluoro-3-nitrooxetane were studied. The polymerization of the glycidyl ether catalyzed by phosphorous pentafluoride was complete within 5 minutes at -78°, and a linear diol with a molecular weight of 1800 was isolated by column chromatography. Only low molecular weight material was obtained with boron trifluoride etherate catalysis. Copolymerization of the epoxide and oxetane took place at ambient temperature with a relatively large amount of catalyst. Preliminary experiments gave copolymers consisting mainly of oxetane-derived units.

An analytical method for functionality determination of oligomeric diols was developed based on NMR measurements of the trimethylsilyl derivatives.

Michael reaction products of nitroform, 1,1-dinitroethane and fluorodinitroethane with methylenemalonic acid esters were prepared and characterized.

CONTENTS

I. Introduction

This report summarizes the research under Contract N00014-78-C-0147 during the period 1 January 1978 through 28 February 1979. This work is a direct continuation of research carried out under Contract N00014-71-C-0176 described in Fluorochem Report No. ONR-1-7, January 1978.

The objective of this program is to develop new synthetic methods for classes of compounds with potential utility in high energy propellants and explosives. Emphasis was continued on studies of the chemistry of 2-fluoro-2-nitro-1,3-propanediol and related compounds, and on polymerization studies of nitrooxetanes and epoxides. A manuscript on Michael reactions of nitro compounds with methylenemalonates comprises Appendix A of this report. The products are potentially useful nitrooxetane intermediates.

Publications during this report period include:

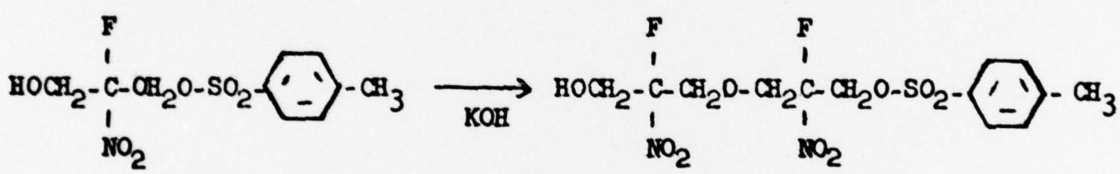
D. A. Lerdal and K. Baum, "Synthesis of Bis(3,3-dinitrobutyl)polysiloxanes", J. Organomet. Chem., 159, 251 (1978).

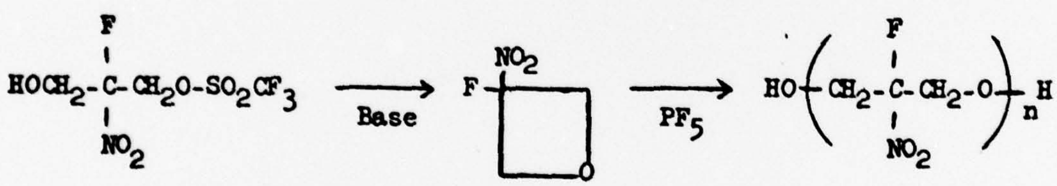
K. Baum and A. M. Guest, "Michael Reaction of Methylenemalonates with Nitro Compounds", Synthesis, in press.

II. Discussion

A. Chemistry of 2-Fluoro-2-nitro-1,3-propanediol

In the preceding report,[1] a practical synthesis of 2-fluoro-2-nitro-1,3-propanediol from diethyl fluoronitromalonate was developed. Reaction of the monotosylate of this diol with base gave the interesting dimer, 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl tosylate, while treatment of the monotriflate of 2-fluoro-2-nitro-1,3-propanediol with base afforded 3-fluoro-3-nitrooxetane. The phosphorous pentafluoride catalyzed polymerization of 3-fluoro-3-nitrooxetane in methylene chloride gave poly (3-fluoro-3-nitro trimethylene ether) as a crystalline solid. The polymer was shown to be a diol of molecular weight 2500.





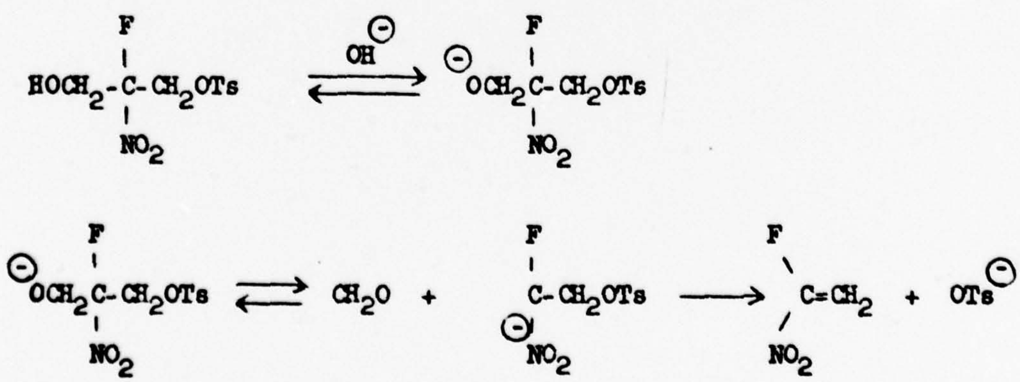
The mechanism of the dimerization of the monotosylate was of interest. The corresponding ditosylate, $C_7H_7SO_2OCH_2CF(NO_2)CH_2OSO_2C_7H_7$, added to the mixture did not take part in the reaction, although the tosylate groups in the two compounds would be expected to be chemically similar. The reaction thus did not appear to be a simple nucleophilic displacement.

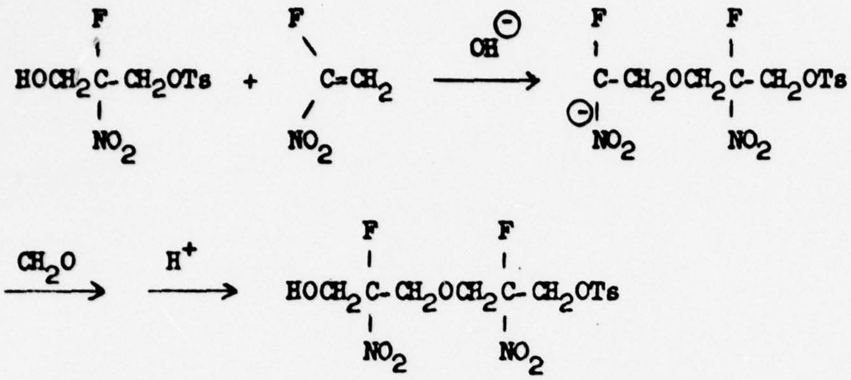
Radical anion intermediates have recently been found to be in-

volved in a number of nitro compound displacement reactions,[2-5] and the possibility was considered for a nitro radical anion activating the tosylate group. However, the usual tests for this mechanism, such as the inhibiting effect of protection from light and the addition of p-dinitrobenzene, did not influence the course of the reaction.

Another mechanism that was considered is the deformylation of 2-fluoro-3-hydroxy-2-nitro-1-propyl tosylate to the nitronate salt. The loss of tosylate ion would give 1-fluoro-1-nitroethylene, which can undergo Michael addition of the alcohol. This mechanism resembles that of 1-bromo-1,1-dinitroethyl acetate reactions in which dinitroethylene is an intermediate.[6,7] The reported absence of deformylation of 2-fluoro-2-nitro-1,3-propanediol in strong base[8] argues against this mechanism.

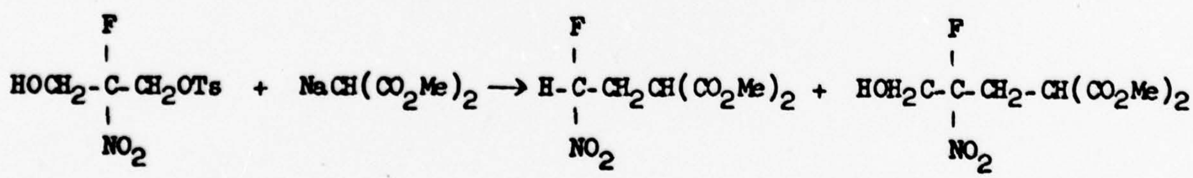
Nevertheless, an experiment was carried out in which an equal volume of formalin was added to a reaction mixture similar to that which gave the dimer. It was reasoned that the loss of formaldehyde in the second step in the sequence below would be inhibited by a mass-action effect of excess formaldehyde.





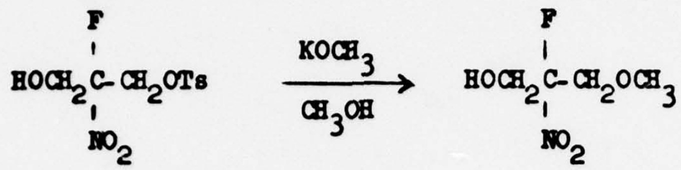
It was found that the addition of formaldehyde resulted in a 75% conversion to dimer in 6 hours, whereas in the absence of formaldehyde, the reaction was 100% complete in 15 minutes. A mechanism involving fluoronitroethylene as an intermediate is also in agreement with the unreactivity of the ditosylate.

Other displacement reactions of the monotosylate were subsequently found that confirmed this reaction course. Thus, when the monotosylate was reacted with five equivalents of the sodium salt of dimethylmalonate in DMF, there was obtained a 22% yield of dimethyl (2-fluoro-2-nitroethyl)malonate and a 5% yield of dimethyl (2-fluoro-3-hydroxy-2-nitropropyl)malonate.



Apparently, most of the formaldehyde generated from the monotosylate is lost by reaction with the excess malonate salt, and a direct addition product of fluoronitroethylene is observed. Also, sodium methoxide in methanol was found

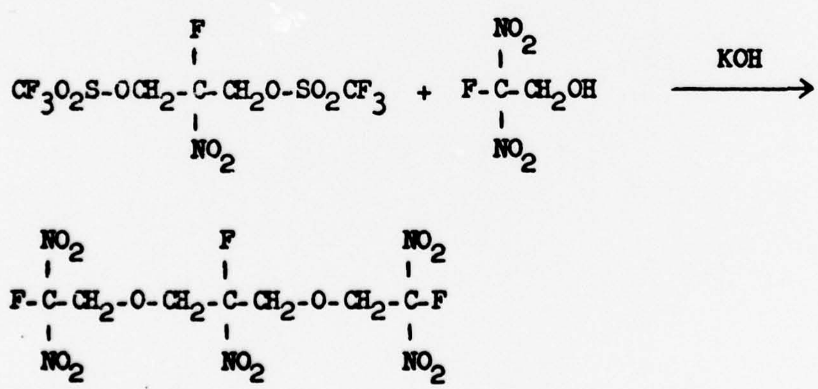
to give 2-fluoro-2-nitro-3-methoxy-1-propanol from the monotosylate whereas the ditosylate was inert. This work is being extended to the exploration of



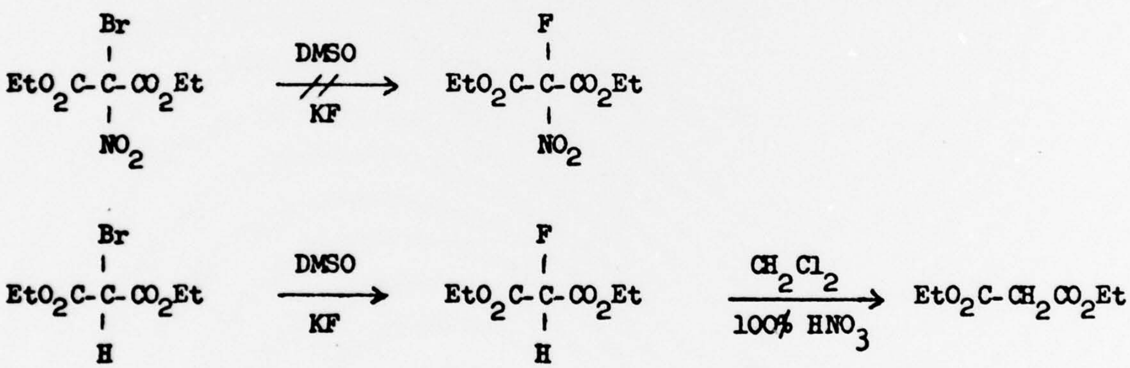
other potentially useful reactions of fluoronitroethylene.

The fact that 3-fluoro-3-nitrooxetane is formed from the monotriflate and not from the monotosylate is attributed to the more reactive leaving group of the former. The initially formed alkoxide cyclizes more rapidly than it can undergo the equilibrium deformylation.

In an effort to define further the reactivity of fluoronitro triflates, 2-fluoro-2-nitro-1,3-propylene ditriflate was reacted with excess 2-fluoro-2,2-dinitroethanol and KOH in dioxane-formalin. A 22% yield of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane was obtained. This energetic ether is a solid, mp 52°C.

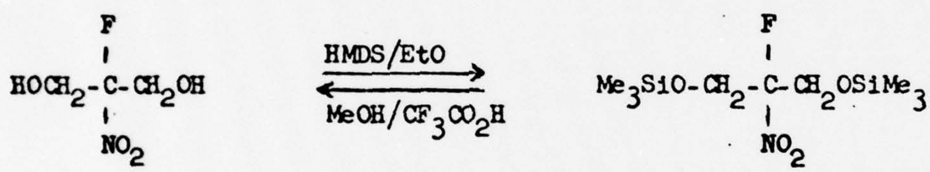


Our preparation of the basic starting material in this area, 2-fluoro-2-nitro-1,3-propanediol, involves the reaction of diethyl fluoronitromalonate with formaldehyde.[1] In order to provide larger quantities of 2-fluoro-2-nitro-1,3-propanediol an improved synthesis of diethyl fluoronitromalonate was desired as well as an improved conversion of the malonate to the diol. Reaction of diethyl bromonitromalonate with two equivalents of KF in DMSO at 100°C for 3 hrs led only to decomposition. However, reaction of diethyl bromomalonate for 15 hrs using the above conditions afforded a 76% yield of diethyl fluoromalonate. An initial attempt to convert diethyl fluoromalonate to diethyl fluoronitromalonate using 100% HNO_3 in methylene chloride failed. Starting material was recovered along with a small amount of diethyl malonate.

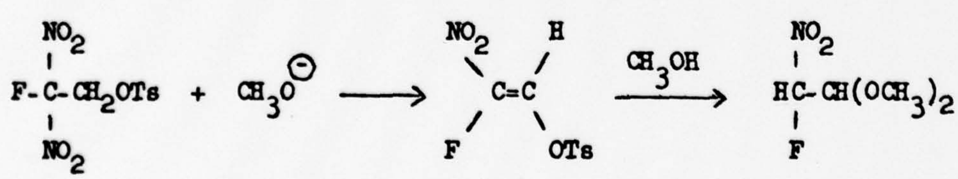


Improvement was obtained in the conversion of the fluoronitromalonate to the diol. It was found that when an ethanolic solution of diethyl fluoronitromalonate was treated with ethanolic KOH at -10°C, followed by the addition of formalin, a 70% yield of 2-fluoro-2-nitro-1,3-propanediol was obtained. An attempt to reduce the ester groups of diethyl fluoronitromalonate with sodium borohydride in aqueous THF to give 2-fluoro-2-nitro-1,3-propanediol was not successful. Only decomposition of the malonate resulted.

Purification of 2-fluoro-2-nitro-1,3-propanediol is difficult because of its high boiling point and tendency to oil during recrystallizations. The use of silyl protective groups was investigated. Reaction of 2-fluoro-2-nitro-1,3-propanediol with hexamethyldisilazane in refluxing ether in the presence of a catalytic amount of ammonium sulfate afforded a 94% yield of 1,3-bis(trimethylsilyloxy)-2-fluoro-2-nitropropane. Treatment of the bis-(trimethylsilyl) derivative with a solution of 5% trifluoroacetic acid in methanol for 2.5 hrs at room temperature allowed recovery of 2-fluoro-2-nitro-1,3-propanediol in 86% yield. The bis(trimethylsilyl) derivative will be used for purification of crude diol.

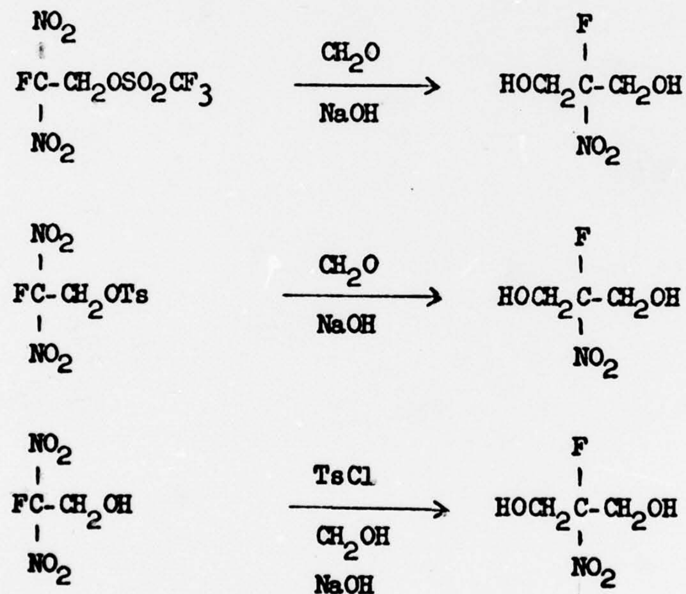


Since 2-fluoro-2,2-dinitroethanol (FDNE) is available in quantity, routes to 2-fluoro-2-nitro-1,3-propanediol from FDNE were investigated. In this connection Adolph[9] reported the following unexpected elimination and addition, as a result of an attempted methoxide displacement of fluorodinitroethyl tosylate.



This sequence would accomplish our desired reduction. Addition of formaldehyde to the CH is facile, and substitution of the blocked aldehyde function

by formaldehyde should be similar to the formylation step in our malonate process. Reactions of both fluorodinitroethyl triflate and fluorodinitroethyl tosylate with solutions of sodium hydroxide in formalin were therefore examined. In both cases the fluorine NMR spectra of the neutralized aqueous solutions essentially showed only 2-fluoro-2-nitro-1,3-propanediol. The process was simplified further by synthesizing fluorodinitroethyl tosylate *in situ*, avoiding its isolation. Thus, tosyl chloride was added to a solution of FDNE in alkaline formalin to give the diol directly.



B. Dinitrooxetane Studies

The successful synthesis of 3-fluoro-3-nitrooxetane led us to investigate the synthesis of the more energetic monomer, 3,3-dinitrooxetane. It was realized that the inhibiting effect of fluorine on the acidity of nitro compounds and on deformylation facilitates the cyclization, but buffering might promote sufficient ionization of the alcohol for cyclization without

effecting deformylation.

The synthesis of 2,2-dinitro-3-hydroxy-1-propyl triflate from 2,2-dinitro-1,3-propanediol and triflic anhydride, was described in our previous report.[1] Its reaction with one equivalent of $NaHCO_3$ afforded only 2,2-dinitro-1,3-propanediol. The same result was obtained when the dinitro triflate was reacted with a $NaHCO_3$-K_2CO_3 pH 9.75 buffer containing only one equivalent of base. Reaction with K_2CO_3 or triethylamine led to decomposition, while reaction with pyridine afforded the corresponding pyridinium salt, as indicated by NMR. By contrast, the reaction of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate with one equivalent of K_2CO_3 in 1:1 aqueous dioxane afforded 3-fluoro-3-nitrooxetane in high yield.

$$HOCH_2-\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}-CH_2OSO_2CF_3 \xrightarrow{NaHCO_3} HOCH_2-\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}-CH_2OH$$

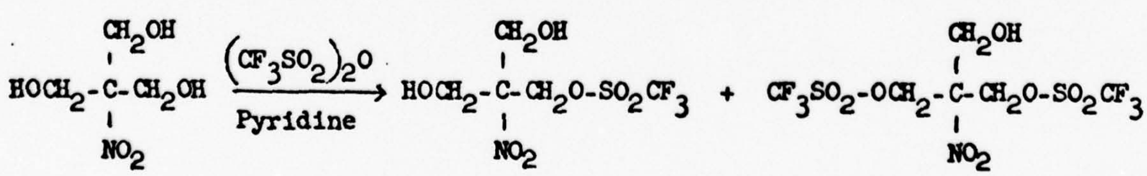
In order to determine if 3,3-dinitrooxetane could be synthesized without the use of base, some model studies were carried out with 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate to simplify product identification. When this monotriflate was refluxed 4 hrs in 1,2-dichloroethane or chlorobenzene in the presence of sodium sulfate, the monotriflate was recovered unchanged. However, reaction of the monotriflate for 5 hrs in nitrobenzene at 165°C led to complete decomposition. When 3-fluoro-3-nitrooxetane was refluxed 4 hrs in chlorobenzene in the presence of sodium sulfate, the oxetane was recovered unchanged. Reaction of the monotriflate with one equivalent of DBU (1,5-diazabicyclo-[5.4.0]undec-5-ene) in ethyl vinyl ether afforded 3-fluoro-3-nitro-

oxetane, indicating that a carbene is not an intermediate.

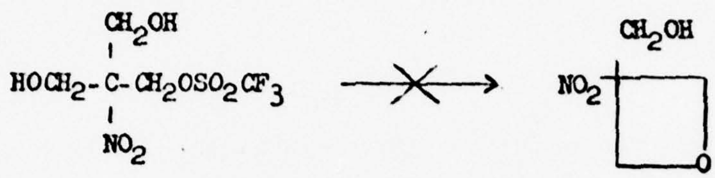
In order to increase the thermal stability and possibly the reactivity of the monotriflate, the corresponding trimethylsilyl derivative was prepared from 2:1 hexamethyldisilazane-trimethylsilyl chloride. After the above silyl derivative was heated at reflux for 15 hrs in carbon tetrachloride and then 2 hrs in chlorobenzene, it was recovered unchanged. Refluxing the silyl derivative for 2 hrs in o-dichlorobenzene led to decomposition of most of the starting material. It is therefore concluded that there is little promise of forming 3,3-dinitrooxetane by thermal ring closure of 2,2-dinitro-3-hydroxy-1-propyltriflate.

Another possible approach to 3,3-dinitrooxetane is from 3-hydroxymethyl-3-nitrooxetane. A mononitro oxetane might be synthesized more readily by ring-closure than the dinitro compound because of less tendency to deformylate. Under more strongly basic conditions, however, 3-hydroxymethyl-3-nitrooxetane should deformylate to afford the nitronate salt of 3-nitrooxetane, which could be converted to 3,3-dinitrooxetane via oxidative nitration.

Reaction of 2-hydroxymethyl-2-nitro-1,3-propanediol in ether-ethyl acetate with one equivalent each of pyridine and triflic anhydride afforded a 12% yield of 2-hydroxymethyl-2-nitro-1,3-propyleneditriflate and a 44% yield of 3-hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate.

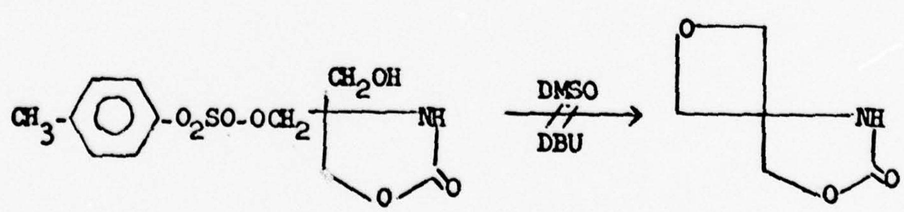


Reaction of 3-hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate in aqueous solution with one equivalent of K_2CO_3 or KOH led only to decomposition. The same result was found when the above monotriflate was reacted in 9:1 methylene chloride-acetone with one equivalent of DBU or triethylamine.



It appears that the ring-closure of the monotriflate of 2-fluoro-2-nitro-1,3-propanediol is a special case, made possible by the ability of fluorine to inhibit nitronate ion formation. Consideration was next given to the synthesis of an aminooxetane, which could subsequently be oxidized to a nitrooxetane. It seemed likely that the ring-closure of a suitably protected 2-amino-1,3-propanediol should be possible.

Such a protected diol is 4,4-bis(hydroxymethyl)oxazolidone, and the reaction of this diol with one equivalent p-toluenesulfonyl chloride in pyridine afforded the corresponding monotosylate in 49% yield. The monotosylate did not react with one equivalent of sodium methoxide in DMSO, and reaction with two equivalents of DBU failed to give the desired oxetane. Reaction of



4,4-bis(hydroxymethyl)oxazolidone with one equivalent each of triflic anhydride and triethylamine or pyridine in either 1:1 DMF-methylene chloride or

9:1 diglyme-ether did not afford the corresponding monotriflate.

In an effort to determine if 3-fluoro-3-nitrooxetane could be converted to other 3-nitrooxetanes, the radical anion reaction of 3-fluoro-3-nitrooxetane with the lithium salt of 2-nitropropane in DMF under nitrogen was investigated. After 6 hours at room temperature, the oxetane was recovered unchanged. Work is being continued on the synthesis of 3,3-dinitrooxetane via oxetane precursors.

C. Polymerization Studies

The polymerization of 3-fluoro-3-nitrooxetane catalyzed by phosphorous pentafluoride was shown in the previous report[1] to give a product with a molecular weight of 2500, a density of 1.59, a DTA exotherm onset of 290°C and a melting point of 234°C.

With the objective of preparing similar polymers with lower melting points, copolymerization studies were initiated. A readily available comonomer for this purpose appeared to be fluorodinitroethyl glycidyl ether, which is prepared by the reaction of FDNE with epichlorohydrin in aqueous alkaline solution.[10] The polymerization of this epoxide has been studied extensively with BF_3 catalysis,[11] and the major problem with this system has been poor functionality without triol initiation. The effectiveness of phosphorous pentafluoride for the polymerization of 3-fluoro-3-nitrooxetane prompted us to investigate its use for the homopolymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether, as well as for copolymerization with 3-fluoro-3-nitrooxetane. This epoxide was found to be considerably more reactive than the oxetane toward PF_5; the epoxide required only a trace of catalyst at -78°, whereas the oxetane required a relatively large amount of catalyst to give

polymerization at ambient temperature.

In the initial experiment, the reaction of 2-fluoro-2,2-dinitroethyl glycidyl ether in methylene chloride was conducted with a catalytic amount of phosphorous pentafluoride for 5 min at -78°C, and the mixture was warmed to room temperature and quenched with methanol. Starting material was consumed completely, and column chromatography separated the product into three components. The material first eluted had a molecular weight (VPO) of 380 and the NMR spectra indicated only $-CH_2-CH-CH_2-O-CH_2C(F)(NO_2)_2$ hydrogens. This material therefore appears to be 2,5-bis(2-fluoro-2,2-dinitroethoxymethyl)-1,4-dioxane. The material next eluted had a molecular weight of 730 and the NMR spectra indicated a trimer, which is capped on one end by a methoxy group. The material last eluted from the chromatography column had a molecular weight of 1100, and its NMR spectrum was consistent with the expected oligomeric diol structure.

The hydroxyl hydrogens of these materials were not observed directly in the NMR spectra. The determination of functionality of oligomeric diols is generally a difficult analytical problem and other laboratories have recently reported conflicting data using standard wet-chemical procedures. We therefore investigated an NMR procedure based on silylation. Trimethylsilylation of hydroxyl groups,

$$ROH + XSi(CH_3)_3 \longrightarrow ROSi(CH_3)_3$$

improves sensitivity by amplifying the number of protons under question by a factor of 9. The silyl protons, unlike hydroxyls, appear in a region of the spectrum free of interfering signals. Traces of water in the sample are converted to volatile, easily removable materials. The feasibility of this

analytical technique was demonstrated with a simple compound having hydroxyls similar to those of the polymer, 3-(fluorodinitroethoxy)-1,2-propanediol, $FC(NO_2)_2CH_2OCH_2CH(OH)CH_2OH$.

The above oligomers of 730 and 1100 molecular weight were trimethylsilylated with hexamethyldisilazane and trimethylsilyl chloride. Integration of the trimethylsilyl protons, compared to the 2-fluoro-2,2-dinitroethyl methylene protons, showed that the original 730 molecular weight material had an equivalent weight (per hydroxyl) of 725, and the 1100 molecular weight material had an equivalent weight of 585. Therefore, within experimental error, the former is a monofunctional alcohol and the latter is a diol.

A change in the reaction procedure that is suggested by these results is the method of quenching; methanol is not desirable. The dioxane might be formed by back-biting of the active cationic end of the polymer, and this reaction could be reduced by not allowing the mixture to warm before it is quenched. The reaction was therefore carried out again for a period of 5 minutes at -78°, and it was terminated by the addition of solid sodium bicarbonate. No starting material remained. Column chromatography separated the polymer mixture into three components, with molecular weights, in the order of elution, of 570, 1070 and 1800. The 570 fraction contained a small amount of 2,5-bis(2-fluoro-2,2-dinitroethoxymethyl)-1,4-dioxane but the bulk of the sample has not been identified. The 1070 fraction showed an equivalent weight by the silylation method of 980, and the material is therefore monofunctional. The 1800 fraction, on the other hand, was found to have an equivalent weight of 935, and is therefore a diol. Thus, an oligomeric diol, in a molecular weight range suitable for polyurethanes, may be pre-

pared and isolated from this energetic and readily available epoxide. Further work is in progress to determine optimum conditions for maximum yield and molecular weight of this product.

We reexamined briefly the use of boron trifluoride etherate to obtain a direct comparison of this catalyst with phosphorous pentafluoride. The reaction of 2-fluoro-2,2-dinitroethyl glycidyl ether in methylene chloride with 10 mole percent boron trifluoride etherate at room temperature was complete within 45 minutes. Only low molecular weight product was obtained, as indicated by TLC. When this reaction was carried out with 1 mole percent boron trifluoride etherate for 5 days, a small amount of starting material still remained, and the same type of low molecular weight product was obtained. With 6 mole percent of boron trifluoride etherate the starting material was consumed over 20 hrs at room temperature, and the same mixture was obtained.

The copolymerization of the epoxide and oxetane was attempted first using the conditions that were effective for the homopolymerization of the epoxide, the more reactive component. When equimolar amounts of 2-fluoro-2,2-dinitroethyl glycidyl ether and 3-fluoro-3-nitrooxetane in methylene chloride were treated at -78°C with a catalytic amount of phosphorous pentafluoride, no reaction occurred. The conditions that gave oxetane polymer were then applied to the copolymerization. When a 2:1 mixture of 3-fluoro-3-nitrooxetane and 2-fluoro-2,2-dinitroethyl glycidyl ether in methylene chloride at room temperature was reacted with excess phosphorous pentafluoride, there was obtained a mixture of both homopolymers and a copolymer. These components were separated by their solubility properties; the copolymer was soluble in acetone and insoluble in methylene chloride, whereas the epoxide polymer was

soluble in both solvents and the oxetane polymer was insoluble. The osmometric molecular weight of the copolymer was 1200. The units of the copolymer derived from epoxide and oxetane are easily distinguishable by fluorine NMR and were in the ratio 1:8. The theoretical molecular weight of a polymeric diol containing one epoxide and eight oxetane-based units is 1196, showing that each polymer molecule contains one epoxy unit. These copolymerization results are preliminary, but it is apparent that the incorporation of a small amount of comonomer can result in substantial changes of solubility properties and melting point.

III. Experimental

2-Fluoro-3-methoxy-2-nitro-1-propanol. To 20 ml of a 1.0 M solution of potassium methoxide in methanol was added 2.93 g (10.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate. After the mixture was stirred at room temperature for 30 min, the resulting precipitate was filtered and washed with methanol. The methanol was removed *in vacuo*, and the residue was taken up in 10 ml of water. The aqueous solution was extracted with CH_2Cl_2 (3 x 15 ml) and ether (2 x 14 ml). The aqueous solution was then adjusted to pH 6 with HCl and extracted with ether (2 x 15 ml). The combined organic extracts were dried over sodium sulfate and stripped *in vacuo* to leave 0.913 g. This residue was chromotographed on 45 g of silica gel, with 50 ml of CH_2Cl_2, 25 ml of 99:1, 25 ml of 97.5:2.5, and then with 650 ml of 95:5 CH_2Cl_2- ethyl acetate. The last 300 ml of eluent contained 0.538 g (35.2%) of 2-fluoro-3-methoxy-2-nitro-1-propanol. Vacuum distillation gave an analytical sample: b.p. 92-93° (0.27 mm); proton NMR ($CDCl_3$) δ 2.92 (broad s, 1 H, -OH), 3.43 (s, 3 H, $-OCH_3$), and 3.8 to 4.3 ppm (m, 4 H, $-CH_2-\underset{NO_2}{\overset{F}{C}}-CH_2$); fluorine NMR ($CDCl_3$) ϕ 140.4 (quintet, J=16 Hz); IR (CH_2Cl_2) 3630 (-OH), 1570, 1355 ($-NO_2$), 1060 cm^{-1} (C-F).

Anal. Calcd fc $C_4H_8NFO_4$: C, 31.39; H, 5.27; N, 9.15. Found: C, 31.50; H, 5.01; N, 8.95.

Dimethyl (2-Fluoro-2-nitroethyl)malonate and Dimethyl (2-fluoro-3-hydroxy-2-nitropropyl)malonate. To 1.32 g (10.0 mmol) of dimethyl malonate in 20 ml of dimethyl formamide was added 0.25 g (10.0 mmol) of sodium hydride. The solution was cooled to room temperature and 0.586 g (2.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate was added. After 17 hrs, the

reaction mixture was diluted with 180 ml of water and then was extracted with methylene chloride (3 x 25 ml) and ethyl acetate (2x 25 ml). The solvents were then removed at 55° (3 mm) and 32° (0.2 mm). The 0.6 g residue was chromatographed on 25 g of silica gel (methylene chloride-ethyl acetate) to give 0.100 g (22.4%) of dimethyl (2-fluoro-2-nitroethyl)malonate: proton NMR ($CDCl_3$) δ 2.4 to 3.1 (m, 2 H, CH_2), 3.60 (t, J=7 Hz, 1 H, $\underline{C}H(CO_2Me)_2$), 3.75 (s, 6 H, CO_2Me), and 5.83 ppm (d of t, J=50 and 5 Hz, 1 H, $H\text{-}\overset{F}{\underset{NO_2}{C}}$); fluorine NMR ($CDCl_3$) 0 146.05 ppm (d of t, J=50 and 20 Hz); IR (CH_2Cl_2) 1740 (CO_2M3), 1575, 1340 (NO_2), 1060 cm^{-1} (C-F). Further elution gave 0.026 g (5.1%) of dimethyl(2-fluoro-3-hydroxy-2-nitropropyl)malonate: proton NMR ($CDCl_3$) δ 2.6 to 3.1 (m, 3 H, $\underline{CH_2}$-CH ($CO_2Me)_2$ and -$\underline{OH}$), 3.53 (m, 1 H, $\underline{CH}(CO_2Me)_2$), 3.73 (s, 6 H, CO_2Me), and 3.8 to 4.5 ppm (m, 2 H, -$\underline{CH_2}$OH); fluorine NMR ($CDCl_3$) ϕ 134.8 (quintet, J=16 Hz); IR (CH_2Cl_2) 3620 (-OH), 1740 (CO_2Me), 1570, 1350 (-NO_2), 1080 cm^{-1} (C-F).

<u>1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane</u>. Potassium hydroxide, 0.665 g (10.0 mmol) was added with ice cooling to 1.545 g (10.0 mmol) of 2-fluoro-2,2-dinitroethanol in 15 ml of 2:1 dioxane-formalin and 1.013 g (2.5 mmol) of 2-fluoro-2-nitro-1,3-propylene ditriflate was added. The temperature rose to 32°C over 6 minutes, and the pH dropped from 11 to 8. After 1 hr, the solvent was removed <u>in vacuo</u>, and the residue was taken up in 5 ml of water and extracted with 50 ml of 1:1 carbon tetrachloride-methylene chloride in three portions. The organic extract was washed with water, dried over sodium sulfate and stripped of solvent to give 0.64 g of a 3:1 mixture of the bis and mono ethers. Chromatography on 25 g of silica gel (2:1 methylene chloride - Skelly F) gave 0.222 g (21.6%) of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane. Crystallization

from methylene chloride - Skelly F afforded an analytical sample: mp 52°; proton NMR (9:1 $CDCl_3$-acetone-D_6) δ 4.2 (d, J=16 Hz, 4 H, $-CH_2-\underset{NO_2}{\overset{F}{C}}-CH_2-$), and 4.70 ppm (d, J=16 Hz, 4 H, $F-\underset{NO_2}{\overset{NO_2}{C}}-CH_2$); fluorine NMR (9:1 $CDCl_3$-acetone-D_6) ϕ 109.4 (broad, 2 F) and 138.7 ppm (quintet, J=16 Hz, 1 F), d_{25}=1.709; IR (CH_2Cl_2) 1600, 1320 cm^{-1} (NO_2).

<u>Anal</u>. Calcd for $C_7H_8F_3N_5O_{12}$: C, 20.45; H, 1.96; N, 17.03. Found: C, 20.47; H, 1.90; N, 16.70.

<u>3-Hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate and 2-Hydroxymethyl-2-nitro-1,3-propylene ditriflate</u>. A solution of 1.9 ml (11.0 mmol) of triflic anhydride in 15 ml of 9:1 ether-ethyl acetate was added dropwise over 15 min at 18-21° (ice cooling) to a solution of 1.51 g (10.0 mmol) of 2-hydroxymethyl-2-nitro-1,3-propanediol and 0.90 ml (11.0 mmol) of pyridine in 30 ml of 1:1 ether-ethyl acetate. The reaction mixture was stirred for 1 hr (water bath cooling) and the precipitate was washed with ether and the ether was stripped <u>in</u> <u>vacuo</u> to leave 3.7 g of a yellow-green mobile syrup. This material was chromatographed on 111 g of silica gel with 4:1 methylene chloride-ethyl acetate to give 0.671 g (16.2%) of 2-hydroxymethyl-2-nitro-1,3-propylene ditriflate and 1.258 g (44.4%) of 3-hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate. An analytical sample of the former was recrystallized from methylene chloride: mp 56-57°; proton NMR ($CDCl_3$) δ 2.70 (broad s, 1 H, -OH); 4.05 (s, 2 H, CH_2OH) and 4.90 ppm (s, 4 H, $CH_2OSO_2CF_3$); fluorine NMR ($CDCl_3$) ϕ 72.4 (s).

<u>Anal</u>. Calcd for $C_6H_6F_6NSO_9$: C, 17.36; H, 1.70; N, 3.37. Found: C, 18.59; H, 1.75; N, 3.64.

An analytical sample of 3-hydroxy-2-hydroxymethyl-2-nitro-1-propyl triflate was recrystallized from methylene chloride - Skelly F: mp 72-73°; proton NMR (acetone-D_6) δ 4.03 (s, 4 H, CH_2OH), 4.47 (s, 2 H, -OH), and 5.10 ppm (s, 2 H, $CH_2OSO_2CF_3$); fluorine NMR (acetone-D_6) ϕ 74.8 (s); IR ($CDCl_3$) 3615 (-OH), 1560, 1360 (-NO_2), 1420, 1225, 1150, 870 (-OSO_2CF_3), and 980 cm^{-1} (C-F).

Anal. Calcd for $C_5H_8F_3NSO_7$: C, 21.21; H, 2.85; N, 4.95. Found: C, 21.02; H, 2.81; N, 4.76.

4-(Hydroxymethyl)-4-p-toluenesulfonatomethyl)oxazolidone. To 1.47 g (10.0 mmol) of 4,4-bis(hydroxymethyl)oxazolidone in 15 ml of pyridine was added, dropwise over 35 min at 5°C, 1.91 g (10.0 mmol) of p-toluenesulfonyl chloride in 15 ml of pyridine. After the solution was stirred 2-1/2 days at room temperature, it was poured into 300 ml of ice-water. The off-white precipitate was filtered and washed with water and ethanol to give 1.48 g (49.1%) of crude product. Crystallization from acetone gave a white solid: mp 187°; proton NMR (DMSO-D_6) δ 2.38 (s, 3 H, CH_3), 3.30 (d, J=6 Hz, 2 H, CH_2OH), 3.93 (s, 4 H, CH_2), 5.07 (t, J=6 Hz, OH), and 7.2 to 7.7 ppm (m, 5 H, C_6H_4 and NH).

2-Fluoro-2-nitro-3-trimethylsilyloxy-1-propyl Triflate. Trimethylsilyl chloride (1.0 ml) was added to a solution of 0.128 g (0.47 mmol) of 2-Fluoro-3-hydroxy-2-nitro-1-propyl triflate in 2.0 ml hexamethyldisilazane. After 2 hrs, a white precipitate was filtered and washed with methylene chloride. Volatile material was removed *in vacuo* to leave 2-fluoro-2-nitro-3-trimethylsilyloxy-1-propyl triflate as a yellow oil: proton NMR (CCl_4) δ 0.12 (s, 9 H, -$SiMe_3$), 3.98 (d, J=14 Hz, 2 H, CH_2OSiMe_3), and 4.85 ppm (d, J=14 Hz, 2 H, $CH_2OSO_2CF_3$); fluorine NMR (CCl_4) ϕ 139.7 (quintet, J=14 Hz).

1,3-Bis-(trimethylsilyloxy)-2-fluoro-2-nitropropane. A mixture of 0.695 g (5.0 mmol) of 2-fluoro-2-nitro-1,3-propanediol, .050 g of ammonium sulfate, 15 ml of hexamethyldisilazane, and 15 ml of ether was stirred at room temperature for 30 minutes, and heated at reflux for 1 hr. Removal of volatile material in vacuo at 45°C gave 1.420 g (93.7%) of crude 1,3-bis-(trimethylsilyloxy)-2-fluoro-2-nitropropane: proton NMR ($CDCl_3$) δ 0.15 (s, 18 H, $SiMe_3$); 3.9 to 4.4 ppm (m, 4 H, CH_2); fluorine NMR ($CDCl_3$) ϕ 141.2 (quintet, J=14 Hz).

Trimethylsilylation of 3-(2-fluoro-2,2-dinitroethyloxy)-1,2-propanediol. A solution of 0.228 g (1.0 mmol) of 3-(2-fluoro-2,2-dinitroethyloxy)-1,2-propanediol in 5 ml of 1,2-dichloroethane was heated at reflux for 2 hrs with 2 ml of hexamethyldisilazane and 0.5 ml of trimethylsilyl chloride. The volatile material was removed in vacuo at 50°C to leave 0.357 g of 3-(2-fluoro-2,2-dinitroethoxy)-1,2-bis(trimethylsilyloxy)propane): proton NMR ($CDCl_3$) δ 0.13 (s, 18 H, $SiMe_3$); 3.3-3.9 (m, 5 H, $O\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O$); 4.57 ppm (d, J=17 Hz, 2 H, $CH_2CF(NO_2)_2$).

Polymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether with phosphorous pentafluoride. A. To a solution of 1.05 g (5.0 mmol) of 2-fluoro-2,2-dinitroethyl glycidyl ether in 11 ml of methylene chloride in a nitrogen atmosphere at -78°C, a catalytic amount of phosphorous pentafluoride was added in the gas phase. After 5 min, the cooling bath was removed, and 15 min later the reaction mixture was quenched with 2 ml of methanol. The reaction mixture was stirred an additional 5 minutes, and solvents were then removed in vacuo to give 1.057 g of a colorless syrup. The molecular weight of this crude polymer mixture, as determined by vapor pressure osmometry (ethyl ace-

tate, 35°C) was 560.

A 0.74 g aliquot of the mixture was chromatographed on 52 g of silica gel (methylene chloride-ethyl acetate) to give, in the order of elution, a 0.174 g fraction of molecular weight 380, a 0.121 g fraction of molecular weight 730, and a 0.122 g fraction of molecular weight 1100.

The MW 380 material was tentatively identified as 2,5-bis(2-fluoro-2,2-dinitroethyloxymethyl)-1,4-dioxane: proton NMR ($CDCl_3$) δ 3.0-4.0 (m, 5 H, $-CH_2-CH-CH_2-O-$), and 4.47 ppm (d, 2 H, J=17 Hz, $O-CH_2-C(F)(NO_2)_2$). The MW 730 material appears to be a trimer, which is capped on one end by a methoxy group: proton NMR ($CDCl_3$) δ 3.1-4.0 (m, 15 H, $-CH_2-CH-CH_2-O$; 3 H, $-OCH_3$), 4.52 ppm (d, J=17 Hz, 6 H, $-C-CH_2-C(F)(NO_2)_2$). The 1100 MW fraction was assigned the oligomeric diol structure: proton NMR ($CDCl_3$) δ 3.2-4.1 (m, 5 H, $-CH_2-CH-CH_2-O-$), and 4.55 ppm (d, J=17 Hz, 2 H, $-O-CH_2-C(F)(NO_2)_2$).

The MW 730 material was dissolved in 5 ml of 1,2-dichloroethane, and 2 ml of hexamethyldisilazane and 0.5 ml of trimethylsilyl chloride were added. After the solution was refluxed for 2 hrs volatile material was removed *in vacuo*. The resulting residue was then dried at high vacuum for several hours. Integration by NMR of the silyl hydrogens, compared to an internal quantitative standard (benzene) or compared to the 2-fluoro-2,2-dinitroethyl methylene protons, showed that the original alcohol had an equivalent weight (per hydroxyl) of 725. The MW 1100 material was shown by this procedure to have an equivalent weight of 585.

B. To a solution of 0.525 g (2.5 mmol) of 2-fluoro-2,2-dinitroethyl glycidyl ether in 5.3 ml of methylene chloride at -78°C, under nitrogen, a catalytic amount of phosphorous pentafluoride was added in the gas phase. After 5 min,

the reaction was quenched with solid sodium bicarbonate. The cooling bath was removed, and after a short period of stirring the reaction mixture was filtered. Removal of the methylene chloride in vacuo left 0.50 g of a colorless syrup.

This material was chromatographed on 25 g of silica gel (methylene chloride-ethyl acetate) to give a 0.182 g fraction of MW (VPO) 570, a 0.107 g fraction of MW 1070, and a 0.108 g fraction of MW 1800. The MW 570 fraction was shown by TLC (methylene chloride) to contain some 2,5-bis(2-fluoro-2,2-dinitroethoxymethyl)-1,4-dioxane. The MW 1070 fraction had an equivalent weight by silylation/NMR of 980, and the MW 1800 fraction had an equivalent weight of 935.

Polymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether with boron trifluoride etherate. A. To 1.06 g (5.0 mmol) of 2-fluoro-2,2-dinitroethyl glycidyl ether (which had been dried by passage through a column of neutral alumina) in 5.8 ml of methylene chloride (also dried by passage through a column of neutral alumina followed by storage over 5A molecular sieves) was added, under nitrogen, 0.062 ml (0.5 mmol) of distilled boron trifluoride etherate. After 35 minutes at room temperature, TLC (methylene chloride) indicated only a trace of the glycidyl ether. After 45 min, solid sodium bicarbonate was added. The reaction mixture was filtered, and the solvent was removed in vacuo to leave 1.045 g of a colorless syrup. As indicated by TLC, this material was a mixture of 2,5-bis(2-fluoro-2,2-dinitroethyloxymethyl)-1,4-dioxane and the low molecular weight oligomer (MW 570) described above. B. To 1.06 g (5.0 mmol) of 2-fluoro-2,2-dinitroethyl glycidyl ether in 5.8 ml of methylene chloride (both components dried as indicated above) was added,

under nitrogen, 0.006 ml (0.05 mmol) of boron trifluoride etherate. After a 5 day reaction period at room temperature, TLC (methylene chloride) still indicated the presence of some starting material. Solid sodium bicarbonate was added. The reaction mixture was filtered, and the methylene chloride was removed _in vacuo_ to leave 0.872 g of a colorless syrup. The TLC of this material was the same found for the above reaction utilizing 10 mole percent boron trifluoride etherate.

Copolymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether and 3-fluoro-3-nitrooxetane. _A_. Phosphorous pentafluoride was bubbled into a solution of 0.260 g (2.15 mmol) of 3-fluoro-3-nitrooxetane and 0.210 g (1.0 mmol) of 2-fluoro-2,2-dinitroethyl glycidyl ether in 5 ml of methylene chloride, under nitrogen, until no more precipitate was formed. After 5 minutes, the reaction was quenched with 2 ml of methanol. After an additional 5 minutes, the precipitate was filtered and was washed with methylene chloride. Removal of the filtrate _in vacuo_ left 0.299 g of a brown syrup. The precipitate was extracted with 25 ml of acetone, leaving 0.070 g of insoluble oxetane homopolymer (NMR identification). Removal of the acetone _in vacuo_ left 0.111 g of copolymer as a white solid: m.p. 178-180°C; MW (VPO; DMF, 65°C) 1200; fluorine NMR (DMF) ϕ 109 (m, 1 F, $\overset{NO_2}{\underset{NO_2}{|}}\!C\!-\!F$), and 140 ppm (m, 8 F, $CFNO_2$).

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Michael Reaction of Methylenemalonates with Nitro Compounds[1]

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The Michael reaction of methylenemalonate esters is potentially useful for introducing difunctionality to organic compounds with acidic hydrogen atoms. The only reported example of this reaction is the addition of diethyl malonate to diethyl methylenemalonate in the presence of potassium hydroxide or piperidine[2,3], and this reaction was complicated by further reaction of the 1:1 adduct with diethyl methylenemalonate.

$$2\,(C_2H_5OOC)_2CH_2 + H_2C{=}C(COOC_2H_5)_2$$

$$\longrightarrow (C_2H_5OOC)_2CH{-}CH_2{-}CH(COOC_2H_5)_2$$

$$\xrightarrow{H_2C=C(COOC_2H_5)_2} \begin{array}{l}(C_2H_5OOC)_2CH{-}CH_2{-}C(COOC_2H_5)_2\\ \qquad\qquad\qquad\qquad\quad\;\, | \\ \qquad\qquad\qquad\qquad\quad CH_2{-}CH(COOC_2H_5)_2\end{array}$$

This multiple addition is a potential difficulty with any Michael reaction of a methylenemalonate, arising from the fact that the product is a monosubstituted malonate with an acidic hydrogen atom. We now wish to report selective additions of nitro compounds to methylenemalonate esters.

The addition of nitroform to diethyl methylenemalonate was carried out by mixing the reagents in aqueous methanol at 0–5° and allowing the reaction to proceed at ambient temperature. An 87% yield of diethyl 2,2,2-trinitroethylmalonate was obtained. Nitroform is a strong acid and is sufficiently ionized that added base is generally not required to promote Michael reactions[4,5].

The reaction of 1,1-dinitroethane with methylenemalonates, however, did not take place under these conditions; this nitro compound is comparable in acid strength with carboxylic acids. The addition of triethylamine to an ether solution of 1,1-dinitroethane and dimethyl methylenemalonate at 0° resulted in the formation of dimethyl 2,2-dinitropropylmalonate in 72% yield.

$$H_3C{-}CH(NO_2)_2 + H_2C{=}C(COOCH_3)_2 \xrightarrow{(C_2H_5)_3N/(C_2H_5)_2O} \begin{array}{l}H_3C{-}C(NO_2)_2\\ \qquad\;\; | \\ \qquad\;\; CH_2{-}CH(COOCH_3)_2\end{array}$$

The addition of fluorodinitromethane to methylenemalonates was carried out in ether solution in the presence of catalytic amounts of pyridine. Diethyl 2-fluoro-2,2-dinitroethylmalonate and dimethyl 2-fluoro-2,2-dinitroethylmalonate were obtained in yields of 82% and 63%, respectively.

$$F{-}CH(NO_2)_2 + H_2C{=}C(COOR)_2 \xrightarrow{pyridine/(C_2H_5)_2O} \begin{array}{l}F{-}C(NO_2)_2\\ \quad\;\; | \\ \quad\;\; CH_2{-}CH(COOR)_2\end{array}$$

$R = CH_3, C_2H_5$

Attempts were also made to prepare these compounds from alkaline 2-fluoro-2,2-dinitroethanol. This reagent is in equilibrium with the fluorodinitromethane anion and formaldehyde and the mixture has been used to synthesize fluorodinitromethane adducts of Michael acceptors, such as acrylates[6]. Under these conditions, methylenemalonates gave complex product mixtures indicative of further reaction of the initial product with methylenemalonate.

Diethyl 2,2,2-Trinitroethylmalonate:

Freshly distilled diethyl methylenemalonate[7,8] (8.0 g, 0.046 mol) is added dropwise with stirring over a 10 min period to a solution of nitroform (16 g, 0.1 mol) in water (25 ml) and methanol (40 ml) at 0–5°. The mixture is stirred for 16 h at room temperature and is then extracted with dichloromethane (100 ml). The dichloromethane solution is washed with 10% sodium hydrogen carbonate and with water, dried over sodium sulfate, and stripped of solvent under vacuum. Column chromatography on silica gel (200 g, eluent: CCl_4/CH_2Cl_2), filtration through charcoal, and removal of solvent gives diethyl 2,2,2-trinitroethylmalonate; yield: 13.0 g (87%); m.p. 24–25°.

$C_9H_{13}N_3O_{10}$	calc.	C 33.44	H 4.05	N 13.00
(323.2)	found	33.36	3.80	12.92

I.R. (neat): $\nu_{max} = 1730$ (C=O); 1600 cm^{-1} (NO_2).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.23$ (q, $J = 7$ Hz, $-C\underline{H}_2CH_3$); 3.80 (m, 3H, $>C\underline{H}-C\underline{H}_2-$); 1.33 ppm (t, 6H, $J = 7$ Hz, $-CH_2C\underline{H}_3$).

Dimethyl 2,2-Dinitropropylmalonate:

Triethylamine is added dropwise to 1,1-dinitroethane (1.6 g, 0.0133 mol) in ether (15 ml) at 0°, until the yellow coloration persists in the solution. The solution is allowed to stand for 1 h at ambient temperature and is then washed with 10% sodium hydrogen carbonate, 1 normal hydrochloric acid, and water. The solution is dried over sodium sulfate and the solvent removed under vacuum. Column chromatography on silica gel (100 g, eluent: CCl_4/CH_2Cl_2) and recrystallization of the product (dichloromethane/hexane, −78°) gives dimethyl 2,2-dinitropropylmalonate as a white crystalline solid; yield: 1.9 g (72%); m.p. 44°.

$C_8H_{12}N_2O_8$	calc.	C 36.37	H 4.58	N 10.60
(264.2)	found	36.66	4.61	10.52

I.R. (neat): $\nu_{max} = 1730$ (C=O); 1570 cm^{-1} (NO_2).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 3.75$ (s, 6H, OCH_3); 3.1–3.5 (m, 3H, $>C\underline{H}-C\underline{H}_2-$); 2.13 ppm (s, 3H, $>C-CH_3$).

Diethyl 2-Fluoro-2,2-dinitroethylmalonate:

Pyridine (0.1 mol) is added over a 5 min period to a solution of diethyl methylenemalonate (8.0 g, 0.047 mol) and fluorodinitromethane[9] (7.0 g, 0.056 mol) in ether (60 ml) at −8° and the mixture is stirred at ambient temperature for 30 min. The solution is washed with 10% sodium hydrogen carbonate and with water, dried over sodium sulfate, and stripped of solvent under vacuum. Column chromatography on silica gel (200 g; eluent: CCl_4/CH_2Cl_2) gives diethyl 2-fluoro-2,2-dinitroethylmalonate as a pale yellow oil; yield: 11.4 g (82%).

$C_9H_{13}FN_2O_8$	calc.	C 36.49	H 4.42	N 9.46
(296.2)	found	36.76	4.29	9.70

I.R. (neat): $\nu_{max} = 1730$ (C=O); 1600 cm^{-1} (NO_2).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.20$ (q, 4H, $J = 7$ Hz, $-C\underline{H}_2CH_3$); 3.2–3.6 (m, 3H, $-CH_2-CH<$); 1.30 ppm (t, 6H, $J = 7$ Hz, $-CH_2C\underline{H}_3$).

^{19}F-N.M.R. ($CDCl_3/CCl_3F$): $\delta = 103.72$ ppm (br s).

Dimethyl 2-Fluoro-2,2-dinitroethylmalonate:

The above procedure using dimethyl methylenemalonate gives dimethyl 2-fluoro-2,2-dinitroethylmalonate as a pale yellow oil; yield: 63%.

$C_7H_9FN_2O_8$	calc.	C 31.35	H 3.38	N 10.45
(268.1)	found	31.70	3.37	11.04

I.R. (neat): $\nu_{max} = 1730$ (C=O); 1600 cm^{-1} (NO_2).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 3.75$ (s, 6H, CH_3); 3.2–3.6 ppm (m, 3H, $-CH_2-CH<$).

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